

## ULTIMATE DISPOSAL OF SCRUBBER WASTES

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### ABSTRACT

Part of the initial concern with using the wet scrubbers on the hypergolic propellants was the subsequential disposal of the liquid wastes. To do this, consideration was given of all possible methods to reduce the volume of the wastes and stay within the guidelines established by the state and federal environmental protection agencies.

One method that was proposed was the use of water hyacinths in disposal ponds to reduce the waste concentration in the effluent to less than EPA tolerable levels. This method was under consideration and even in use by private industry, municipal governments, and NASA for upgrading existing wastewater treatment facilities to a tertiary system.

At the present, Battelle Memorial Institute, National Space Technology Laboratories/NASA, and Florida Institute of Technology feel the use of water hyacinths in disposal ponds appears to be a very cost-effective method for reduction and disposal of hypergolic propellants.

## ULTIMATE DISPOSAL OF SCRUBBER WASTES

Part of the initial problem with using the wet scrubbers on vented hypergolic propellants was the ultimate disposal of the liquid scrubber wastes. Hence, consideration was given to all possible methods of reducing the amounts of nitrogen in the wastes to stay within the guidelines established by the state and federal agencies. These guidelines require that the total Nitrogen discharged to any body of water be no more than 5.0 ppm.

One proposed method was the use of water hyacinths in disposal ponds to reduce the waste concentration in the effluent to acceptable levels. It was postulated that hyacinths may absorb  $\text{NO}_3^-/\text{NO}_2^-$  from  $\text{N}_2\text{O}_4$  scrubber wastes.

A literature search was made preliminary to initiation of test runs in the Prototype Disposal Pond at KSC or at FIT to acquire a better background on the bioassimilation method for removal of pollutants from water.

At the present, operational waste water treatment plants utilizing water hyacinths as part of a functional design are in use by private industry, municipal governments, and NASA. These uses include new facilities and the upgrading of existing waste water treatment plants to a tertiary system. Examples are: General Development Corporation, Palm Bay, Fl, Disneyworld, Lake Buena Vista, Fl., and NASA, National Space Technology Laboratories, Bay St. Louis, Miss.

This is, in fact, not a new concept. Suggestions for this application date back at least to the 1940's, but recent emphasis on

on improved water quality has created a situation in which the hyacinth's capabilities have great potential value.

The approach to utilizing water hyacinth for absorption of oxidizer and fuel wastes is to introduce the diluted wastes into PVC-lined ponds, of proper size and depth, the surface of which is covered with a mat of hyacinth plants. Several favorable characteristics of the hyacinth exist which make it attractive for this purpose. For example, the high absorption capability for nitrogen-containing compounds for rapid depletion of pollutants, its rapid growth rate, the ability to withstand relatively high concentrations of the toxic materials, the ability to service a wide pH range of 4 to 10, together with the relative ease of harvesting the large, free-floating plants have made the water hyacinth an attractive plant choice for this purpose.

To understand the use of hyacinths, one must know about the plants and its characteristics.

The water hyacinth (Eichornia crassipes) is a flowering aquatic plant found in waterways of tropical and semitropical areas around the world. It currently grows throughout Florida, in southern Georgia, Alabama, Mississippi, Louisiana, and in parts of Texas and California. The plant is sometimes found rooted in soil, but more commonly is free-floating, drawing nutrients from the water. The individual plants are of moderate size, measuring perhaps 50 cm from root tip to the top of the flower cluster. Typical weight is 1 kg, of which 95 percent is water.

The hyacinths have been designated a noxious weed by the federal government because of the plant's tendency to form dense mats. which interfere with most waterway uses. Under favorable growth conditions, spreading of hyacinths mats can be extremely rapid, doubling total plant mass in periods of a few weeks.

The disposal pond size requirement is dependent on several factors. The first factor is the quantity of each pollutant to be disposed of per unit time. The pond size will be directly proportional to the total amount of hypergolic wastes generated at KSC which have to be treated. The pond size will further depend on maintaining the concentrations of the wastes in the pond water to below the harmful limits of each waste. The "safe" limits for both  $N_2O_4$  and MMH wastes were established by trial runs in 50 gal. tanks. An advantage arising by simultaneous treatment of both wastes is one of economy. Less chemicals for pH adjustment is required as a result of the self-neutralizing feature. In very dilute solution no odor problems were observed nor are other problems, as chemical burns, animal deaths, etc., expected.

The second factor, the degree of pollutant removal required, may have a significant effect on pond size. The more stringent the liquid effluent requirement adopted, the larger the pond area or the longer detention time will be necessary for reducing pollutant concentration to acceptable limits prior to discharging the pond water to surface water or to ground disposal.

The third factor, hyacinth growth rate was obtained from literature for central Florida estimating a minimum of 10 to a high of 80 tons dry weight per hectare year. Hyacinth growth rate is not uniform the year round. In central Florida a short period during winter may occur in which

growth is slow due to freezing air temperature.

Temperature is of paramount importance in the design of a pond system. It affects photosynthetic  $O_2$  production, hyacinth growth rate, as well as other biological reactions. The optimum temperature range for maximum hyacinth growth rate is  $22-27^{\circ}C$ . Limiting lower and upper values were reported to be  $2^{\circ}C$  and  $35^{\circ}C$ , respectively.

When the water temperature decreased to freezing, the hyacinths are highly susceptible to damage or death. A similar situation occurs when water temperatures approach  $35^{\circ}C$ . At that point, the beneficial algal population will be severely curtailed. Such high temperatures were not observed at the disposal pond during the time of testing.

Light intensities are relatively high in mid-Florida, even during winter months. Hyacinth growth or development is slowed during winter months, consequently reducing the permissible loading per unit pond surface area at this time. If pond loadings are maintained below critical levels so that hyacinth development and the resultant photosynthetic activity maintains aerobic conditions, then water stabilization and nitrate removal can be still effective in winter. The amount of stabilization achieved in winter is  $1/3$  or less the summer rate in central Florida.

Except for a period of approximately four months in winter, when activity is at its lowest, hyacinth activity is both directly and indirectly responsible for other changes besides oxygenation. The photosynthetic plants are responsible for elevating the pH of the water permitting nitrification with the escape of  $NH_3$ . All pond systems have an excellent buffering capacity for balancing out excessive peak loads and extreme pH variations. Various nutrients such as phosphates and trace metallic elements are simultaneously embodied in the plant cells.

Thus, if the hyacinths are periodically harvested, the  $\text{NO}_3^-/\text{NO}_2^-$  content, metallic constituents and nutrients of the water are accordingly reduced. It appears, therefore, that as long as a pond remains aerobic, climatic changes have an effect on water purification.

In addition to seasonal changes, the nutrient content of hyacinth varies with location and water quality. The Kjeldahl  $\text{N}_2$  of hyacinth plant from the disposal pond vs a natural plant as a control were found to be 1.96% vs 1.53%, respectively, based on air dried plants.

The essential role of the hyacinth is its ability to assimilate the nitrogen compounds. Previous research demonstrated a high removal of  $\text{NH}_4^+$  and  $\text{NO}_3^-$ -nitrogen from waters in which the hyacinths were growing in the laboratory and in farm ponds. The rate of  $\text{NO}_3^-$  ion uptake was shown to be slower than  $\text{NH}_4^+$  ion.

The mineral content of water hyacinth varies with location. Significantly, considerable absorption of some heavy metals, as Fe, Pb, Cr and Cu occurs during the growth of the plant. At NSTL, with the addition of Cadmium to their disposal ponds, there was a reduction of 60% within the first day. This fact can be of interest from the standpoint of providing an alternative means for disposing of the unwanted metallic constituents in plating wastes or miscellaneous chemical wastes. Further, it is believed that simultaneous treatment of hypergolic wastes and heavy-metal containing wastes in a common pond is feasible after suitable dilution.

As will be discussed later, the total nitrogen content at the end of one experimental run was reduced from 118 ppm to 2.68 ppm. This value is below the Florida Department of Pollution Control Regulation, Chapter 17-3

criterion for an advanced waste water treatment effluent. Thus, it would be permissible to discharge the pond effluent directly to the ground or a receiving body of water.

The effect of the residual nitrogen on the receiving body of water would be minimal and no worse than the effect from the discharge of secondary effluent now permitted into streams from typical sewage treatment plants.

The estimated costs of these systems can be expected to vary over a wide range, depending on a number of local and particular circumstances. In some cases, lagoons may already be available. In others, adequate land may already be owned by the operating authority. Also, it may be that lagoon construction costs might be cut substantially by use of a labor force from various municipal organizations.

For cost comparison purposes, it was decided to assume that completely new facilities were to be engineered and constructed, with full market prices to be paid for land, equipment, and services. The cost estimates included both operating costs and annualized capital costs. The principal elements are:

- a. Land acquisition
- b. Engineering
- c. Construction
- d. Interest
- e. Labor costs, both direct and indirect
- f. Maintenance and administrative costs, and materials and supplies

A cost comparison was made between the construction of hyacinth-based and other waste water treatment systems.

In central Florida, where the hyacinth system can operate year-round, it offers the possibility of meeting all the effluent requirements at a cost of about \$.50/1000 gallons. Whereas the hybrid design system will meet all the effluents requirements at a cost of about \$.89/1000 gallons. This suggests that the hyacinth system has an appreciable cost advantage, even using full costs.

If land is already owned, or if lagoons are already in existence, hyacinth system costs can be further reduced. In the case of the hyacinth design, if the capital cost can be reduced to a nominal amount the overall cost would be reduced some 20 percent, bringing the cost per 1000 gallons to approximately \$.40 in central Florida. This is less than half the cost of the conventional system.

These cost estimates are from reports by NASA's National Space Technology Laboratories and Battelle Memorial Institute.

To prepare the experimental disposal pond, a site was chosen away from any flood areas. The bottom of the pond pit was sloped to allow for draining. The ground was chemically treated to prevent growth of trees or other vegetation. In the graded excavated pit, a hypalon unreinforced liner was installed. This liner was to prevent leaching out of pollutants from the system. Refer to Figure 1.



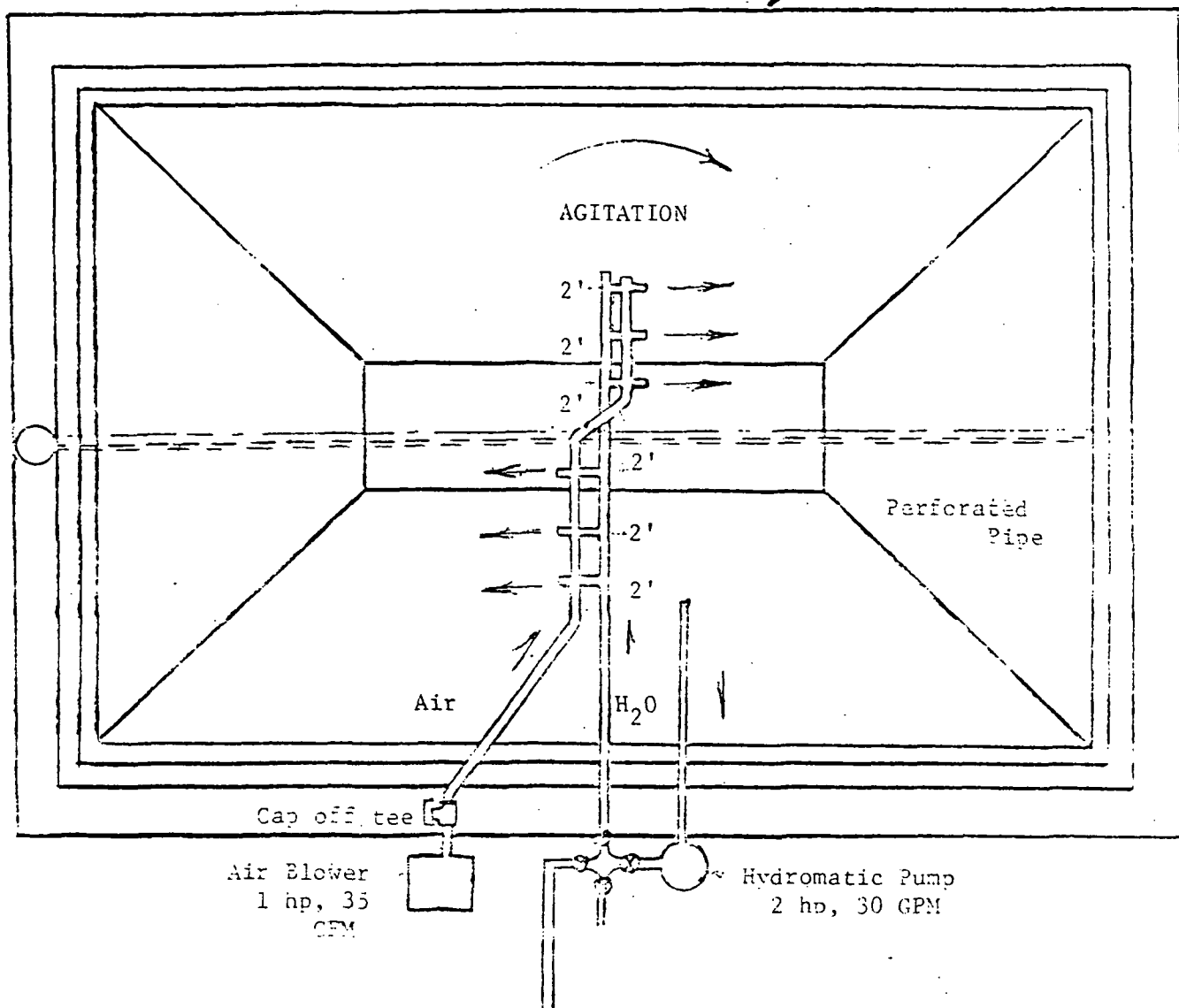


Figure 1. Schematic of Pond.

The pond was situated conveniently with respect to a supply of water and electrical power for operating pumps and air blowers. The water circulation pump was designed to prevent an anaerobic condition from developing by an occasional turnover of the bottom water layer so as to keep the organic debris in suspension or accessible to dissolved oxygen. The air blower was installed to provide supplemental oxygen to the system. The dimension of the pond is 24 x 36 feet with an operating liquid volume of 9000 gallons. Refer to Figure 2.

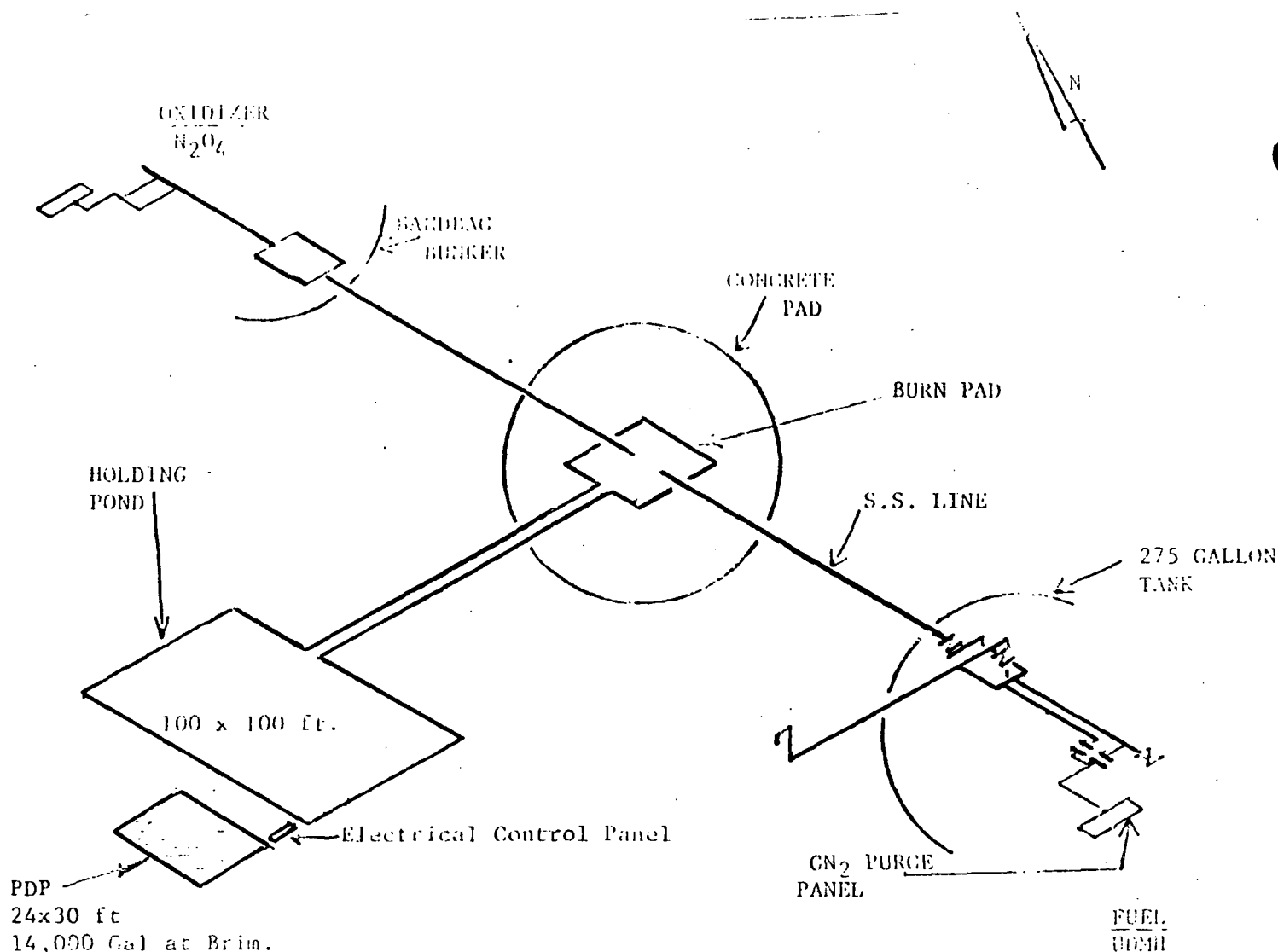


Figure 2. Pond Layout in Fire Suppression Training Area.

Prior to conducting any experimental runs, it was necessary to provide a suitable chemical and biological environment to ensure adequate growth and health for the hyacinths. The following describes the preparation.

To 8600 gallons of water in the disposal pond, algae inoculum nutrients, and trace elements were added. The algae inoculum consisted of two gallons of fresh aerobic digester sludge from a sewage water treatment plant. In addition to the algae, the sludge contained the biota usually found in this material which was necessary for establishing a balanced ecological system.

In addition to these elements, trace quantities of other elements may be expected to occur from the impurities of the chemicals as well as from the dissolved and suspended materials naturally present in the water used to fill the pond.

Four days were allowed for the pond to come to chemical and biological equilibrium prior to stocking with hyacinths. After stocking, two days were allowed to acclimate the plants to the new surroundings.

The objectives of Run #1 ( $\text{N}_2\text{O}_4$ /hyacinth) are:

- (1) to determine the fall-winter  $\text{NO}_3/\text{NO}_2$  uptake rate of water hyacinths.
- (2) to discover potential problem areas in operating such a pond
- (3) to observe the feasibility of utilizing hyacinth as a method for destroying  $\text{N}_2\text{O}_4$  wastes.

After preparing the pond as described in the previous section, Run #1 was started on November 11, 1976, which was 0-day for timing purposes. On this day, first a circulatory motion was established in the pond by means of the jet eductors. Then four liters of pure  $\text{N}_2\text{O}_4$  were slowly introduced over a two hour period to minimize local pockets of high  $\text{NO}_3/\text{NO}_2$  concentrations which could seriously damage the plants.

Prior to adding the  $\text{N}_2\text{O}_4$ , pH was 9.9 on Nov. 11, 1976. After addition the pH dropped drastically to 3.6. As a result of this low pH the algae in the pond were severely damaged and practically disappeared in all but isolated pockets. The hyacinth survived this treatment without any visible damage. At the next sampling date a week later, however, the pH had risen to 6.0 as a result of the natural buffering action of the plants in the pond. The algae population started to multiply rapidly. After another week pH had risen to 9.4. At this time a pH adjustment was made by addition of  $\text{Na}_2\text{HPO}_4$  and  $\text{H}_3\text{PO}_4$  for two purposes.

One, to decrease pH to the more favorable natural level and two, to increase phosphate to approximately the 20 ppm level. Henceforth, pH changes were within several tenths of the neutral point (the pH preferred by hyacinth).

Water samples were taken at weekly intervals or more frequently for the duration of the run to follow the progress of nitrogen uptake and other changes. The sample consisted of an integrated 1 gallon of water collected from 10 equidistant points around the perimeter of the pond, 6 or more inches below the water surface. On the spot analysis of dissolved oxygen was performed on a top and bottom water sample. These data were used in interpreting the results. Analyses on the collected sample were performed at FIT on the same day or samples were stored in a refrigerator at 4°C for the next day. The test methods used were as given in "Standard Methods, Water and Waste Water" 13th edition. Refer to Chart 1.

Chart 1. Analytical Data for Run #1 PDP

Days	NO <sub>3</sub> <sup>-</sup> (ppm)	NO <sub>2</sub> <sup>-</sup> (ppm)	NH <sub>4</sub> <sup>+</sup> (ppm)	Total Nitrogen	O-PO <sub>4</sub> (ppm)	D.O. (mg/l)	pH	Turbi- dity F.T.U.	True Color
0	462	41.25	0.67	118.05	2.9	----	3.6	25	50
+12	392	24.75	4.45	100.15	4.0	T:6.0 B:3.5	9.4	35	51
+20	348	18.98	2.60	86.90	21.3	9.5	7.6	30	5
+27	312	16.50	1.50	77.20	20.5	T:7.6 B:7.2	7.3	40	20
+40	255	0.12	0.44	58.40	18.50	T:8.4 B:6.2	6.9	20	20
+50	275	0.83	4.60	66.50	17.50	T:9.4 B:4.2	6.9	15	35
+57	9	0.03	0.32	2.27	15.50	T:11.4 B:8.6	7.5	25	5

The NO<sub>3</sub><sup>-</sup> uptake by hacinth in the disposal pond during the winter period of mid-Nov. 76 to mid-Jan. 77. The results show an initial slow decrease in NO<sub>3</sub><sup>-</sup> from the 462 ppm peak level to approximately the 280 ppm level in a 50 day period, then a rapid decrease to the 10 ppm level in the succeeding 8 day period, and finally a very slow drop to the 6 ppm level occurring in the next 16 days. At this point the run was terminated. The 10 ppm level was arbitrarily selected as a target to indicate completion

of a run. Fluctuations of the  $\text{NO}_3^-$  in or about this level will occur naturally due to the decomposition of proteinaceous materials in the organic detritus. The rapid  $\text{NO}_3^-$  uptake occurring in the 8 day period was partly attributed to the observed algal bloom. The very slow uptake occurring in the last stage can be accounted for by the after effects of the near freeze and the freeze which caused a die back of the hyacinth plants. The subsequent decomposition of dead plant tissues releases a small amount of  $\text{NO}_3^-$  salts into the pond water.

The rate of  $\text{NO}_3^-$  absorption during the winter months in Run #1 was found to be 64.4 lbs.  $\text{NO}_3^-$  per acre day in a pond containing approximately 3-1/2 feet of water with an average 70% hyacinth coverage.

It is evident that the  $\text{NO}_2^-$  was reduced from a peak of 41 ppm to below 1 ppm then rose to 4.5 and dropped to below 1 ppm after 57 days. The  $\text{NO}_2^-$  was reduced to the low level at about the same time as  $\text{NO}_3^-$ .

A second  $\text{o-PO}_4$  addition was made to the pond on 12-2-76 in order to increase the concentration to a preferred level. A slow decrease in  $\text{o-PO}_4$  is shown for the duration of the run.

The amount of  $\text{NH}_4^+$  was increased from almost nil up to the 4.5 ppm level in about a 6-day period then dropped to below 1 ppm and finally increased to about 12 ppm at the 57th day. This increase is related to the die-back of the hyacinth as a consequence of the cold snap occurring at the same time.

A near kill of the algal population resulted after the introduction of 4 l  $\text{N}_2\text{O}_4$  into the pond in order to increase the  $\text{NO}_3^-/\text{NO}_2^-$  concentrations desired from the existing temporary levels of 228 ppm/0.27 ppm to the final

desired levels of 462 ppm/41 ppm respectively. The hyacinth survived this shock addition with minimal visible effect. After one or two weeks the algal population reappeared in large numbers.

At the start of Run #1 the pond was initially filled to contain approximately 8,600 gallons of water. Chloride ( $\text{Cl}^-$ ) picked up by hyacinth is considered to be minimal. Therefore, the  $\text{Cl}^-$  concentration in the pond water was used to monitor the water level. The  $\text{Cl}^-$  remained essentially the same from start to finish of the run. The small variation shown is considered an experimental error with our method of analysis. Thus, the  $\text{Cl}^-$  concentration does not show either a dilution effect that can be attributed to rain or an evaporation effect, i.e. the volume of water was fairly constant during the run.

The  $\text{NO}_3^-$  was increased to 462 ppm; the apparent free  $\text{Cl}_2$  rose to above .6 ppm. Then, as  $\text{NO}_3^-$  decreased to 253 ppm, the apparent  $\text{Cl}_2$  decreased to .02 ppm. For this reason the tests for free  $\text{Cl}_2$  were discontinued since they have no significance. Two hyacinth stockings were made, first on Nov. 14, 1977, second on Nov. 18, 1976, resulting in 60% coverage. Due to plant growth and a small increase in the number of plants the coverage increased to approximately 85% near the end of the run.

The occurrence of freezing weather in the 2nd week of January resulted in severe damage. Approximately 90-95% of the exposed parts of the plants turned brown. Patches of ice were observed on the pond surface

and the water temperature was at the freezing point. The cold snap coincided roughly with the end of the run on the 57th day. However, data collection was continued until January 21. Hyacinth coverage was difficult to judge but estimated at about 10%.

The turbidity in water is caused by the presence of suspended matter, such as clay or inorganic or organic matter. The increase in turbidity was due almost entirely to the increase in the population of algae rather than from suspended solids. Turbidity increased from 18 FTU to a high of 52 then decreased to 19 on the 57th day. As the nitrogenous compounds were used up, turbidity dropped to about the original level. Color in water may result from the presence of humus, plankton, weeds, etc. True color, as used herein is the measurement obtained from the sample from which turbidity has been removed by means of centrifugation. Apparent color is determined on the original sample without any pretreatment. True color fluctuated rather widely. Apparent color reached a peak coinciding with that of turbidity, which then decreased. Both measures decreased toward the end of the run.

The analysis of dissolved oxygen (DO) is a key test in water pollution control activities. The samples taken either from four inches below the water surface or from the bottom of the pond. The latter samples were obtained by means of a sampler assembly used for this purpose.



Measurements were made on site because of the instability of the samples on storage. Both D.O.'s roughly parallel each other. The water temperatures were taken for certain samples. The lowest bottom reading obtained was 3.5 ppm, the highest top sample reading was 12.1 ppm obtained on Nov. 16, 1976. The lower than normal air temperature during Run #1 probably explains the higher than expected D.O. level found in the pond containing a mat coverage of up to 80%.

The D.O. level is an important consideration in maintaining the desired aerobic conditions in the pond.

The Nitrogen-Phosphorus Ratio (N/P) was 125 immediately after adding  $N_2O_4$  to the pond, but within 6 days decreased to 69. An addition of  $NaHPO_4$  and  $H_3PO_4$  was made on the 12th day. From the 14th to the 50th day the ratio did not vary greatly. However, the ratio was sharply reduced during the algal bloom period and was decreased to about the .5 level for the duration of the run which extended to the 72nd day. During the algal bloom period the  $NO_3^-$  was reduced to the 10 ppm or lower level by the hyacinth-algae.

Chart 2. COD Results on Filtered Sample  
From PDP

Days	COD mg/l	Agit/n.Agit	Comments
0	69.5	AGIT	
6	44.4	NA	
6	46.3	AGIT	
6	24.3	NA	Large KSC Pond
6	19.3	-	KSC Tap $H_2O$
12	38.6	SHORT AGIT	
14	42.4	AGIT	
20	38.6	NA	
23	Not tested	AGIT	

The Chemical Oxygen Demand (COD) determination provides a measure of the oxygen equivalent of that portion of the organic matter in a sample that is susceptible to oxidation by a strong chemical oxidant. It is an important parameter in stream and industrial waste studies. Refer to Chart 2.

The change in COD is a slow decrease from about 89 mg/l to 42 mg/l over a 10 week period. Filtered samples were used in the test to remove the large amount of algae present in the pond water. Therefore, the results reflect only that portion of soluble organic or oxidizing matter that was present in the filtrate. Interpretation of these data is inconclusive since a correlation with uptake of any nutrient, hyacinth coverage or other easily observable relationship could not be found. Consequently, COD testing was curtailed after the 12th water sample.

This run showed that various forms of soluble nitrogen-containing material in the pond water were bioassimilated by the aquatic biota. The major TN absorbed was attributed to the hyacinth because of their larger biomass. The fall uptake rate was 16.4 lbs TN/acre-day.

Of great importance, it was shown the feasibility of the moving soluble  $N_2$  compounds (up to 460 ppm  $NO_3^-$ ) from water by hyacinths existed.

It was estimated that the disposal pond had a maximum resident population of approximately 3760 hyacinth plants at the end of Run #1. The increase from the initial 50% mat coverage to the final 75% coverage after a 6 weeks period was attributed mostly to increase in plant size rather than any substantial increase in the number of new plants.

Run #4 was set up and performed with objectives similar to Run #1 except the ratio of  $\text{NO}_2^-$  to  $\text{NO}_3^-$  was considerably higher than in Run #1, and the volume of water was greater. Again, upon the addition of pure  $\text{N}_2\text{O}_4$  it was not neutralized. The sampling and analytical procedures utilized were similar to those described for Run #1. The purpose of Run #4 was to determine the results for winter. A second purpose was to observe the effect of a high  $\text{NO}_2^-$  concentration on hyacinths. The pH was maintained above 6.0 during addition of the  $\text{N}_2\text{O}_4$  by adjustment with NaOH solution.

The condition of the hyacinth in the pond at initiation of Run #4 was fair to poor. The plants were recovering from the effects of the freeze which occurred a few weeks previously.

A freeze or near freeze occurred on February 17, 1977, causing severe damage to the hyacinth.

Chart 3. Analytical Data for Run #4 PDP

Days	$\text{NO}_3^-$ (ppm)	$\text{NO}_2^-$ (ppm)	$\text{NH}_4^+$ (ppm)	Total Nitrogen	O- $\text{PO}_4$ (ppm)	D.O. (mg/l)	pH	Turbi- dity F.T.U.	True Color
0	135	33.00	1.16	40.7	19.3	---	6.3	28	30
5	121	13.20	1.34	31.5	18.5	T:12.6 B:4.2	6.7	32	75
13	37	0.17	1.34	8.6	18.5	T:7.4 B:4.0	6.5	40	75
27	16	0.40	1.65	4.2	16.5	T:6.4 B:2.5	6.8	30	100
33	16	0.15	2.20	3.8	18.0	T:11.4 B:2.8	7.2	28	100
40	17	0.11	1.71	3.6	---	T:9.25 B:4.75	7.0	--	---

Six water samples were taken during the run. For purposes of calculating the nitrogen uptake rate, run duration was set at 35 days though data was collected for 40 days. The  $\text{NO}_3^-/\text{NO}_2^-$  were reduced from the 135/33 ppm to the 17/.11 ppm levels, respectively. Refer to Chart 3.

The TN was reduced from 40.7 to the 3.6 ppm level;  $\text{O-P}_4$  decreases slowly with time. Turbidity increases from 28 to 40 then decreases to 28 FTU.

The coverage of live plants was reduced to about 10% after the freeze of Feb. 17 due to the poor initial condition of the plants combined with adverse cold weather periods. The rate of nitrogen absorption from the pond was greatly reduced.

The comments made in Run #1 apply as well to Run #4 for the following tests: pH,  $\text{Cl}^-$ , MMH, color, and D.O. The differences are those of degree and of not too much consequence.

The  $\text{NO}_2^-$  concentration in Run #4 was 33 ppm compared to 41 ppm in run #1. No pronounced toxicity effects, at least easily observable effects, were noted on the hyacinth due to the high  $\text{NO}_2^-/\text{NO}_3^-$  ratio. The algae may have suffered a slight decrease immediately after  $\text{N}_2\text{O}_4$  addition, but at the next sampling period, a week later, the algae appeared to be unaffected.

Due to the cold temperature during Run #4, damage occurred in the 3d week into the run, resulting in low nitrogen uptake. The TN uptake rate was calculated to be 9.76 lbs/acre-day.

Thus, the TN uptake rate was lower in run #4 than in run #1 in which a rate of 16.6 lbs/acre-day was obtained.

The experiences with Runs #1 and 4 provides useful design information. Also, one is able to predict that a hyacinth recovery period of several weeks may be necessary for new growth and damage repair in winter

months. In the event of a hard freeze in central Florida, which is unlikely, it is conceivable for extensive irreparable damage to occur, necessitating hyacinth restocking.

The winter rate of TN uptake is strongly dependent on air temperature. A rate of about 10 lbs/acre-day may be expected in the event of a mild freeze that damages the leaves of the hyacinth; or considerably less if both leaves and roots are damaged.

If a freeze factor is incorporated into the design equations for the hyacinth pond-disposal system, the TN uptake would be increased.

Run #A-3 was set up and operated with objectives similar to Runs #1 and 4, primarily to determine the spring  $\text{NO}_3^-/\text{NO}_2^-$  uptake rate of water hyacinth. The  $\text{N}_2\text{O}_4$  was added and again not neutralized.

The general condition of the weather had improved with a warming trend. The hyacinths were in good shape at the initiation of Run #A-3.

During the run, a total of five samples were taken over a duration of 19 days. Refer to Chart 4.

Chart 4. Analytical Data for Run A-3 ( $\text{N}_2\text{O}_4$ /Hyacinths)

Days	$\text{NO}_3^-$ (ppm)	$\text{NO}_2^-$ (ppm)	$\text{NH}_4^+$ (ppm)	Total Nitrogen	O- $\text{PO}_4$ (ppm)	D.O (mg/l)	pH	Turbi- dity F. T. U.	True Color
0	282.	116	--	97	28.0	--	5.4	120	70
1	262.	114	--	95	27.2	--	5.6	--	--
7	142.	56	--	51	22.5	--	7.3	120	74
13	43.	23	--	18	17.0	--	7.1	150	100
19	0.13	0.02	--	1	20.8	--	6.8	85	96

The  $\text{NO}_3^-/\text{NO}_2^-$  were reduced from 282 to 0.13 ppm and 116 to 0.02 ppm, respectively.

The TN was reduced from 97 to 1 ppm, and the  $\text{O-PO}_4$  decreased at a slow rate compared to TN rate.

The turbidity and true color increased with the algal growth present and decreased as the  $\text{NO}_3^-/\text{NO}_2^-$  were utilized.

The plants were maintained at approximately 80% coverage. As the rapid uptake of  $\text{NO}_3^-/\text{NO}_2^-$  occurred, an extreme rate of growth required weekly harvesting of the hyacinths which displayed a rich, green, healthy color. The weekly harvest reduced the coverage from 90-95% back to 80%.

The spring TN uptake rate was calculated to be 41.5 lbs/acre-day.

Run #C-1 was set-up and performed primarily with the objective of determining the summer  $\text{NO}_3^-/\text{NO}_2^-$  uptake rate of water hyacinths. Similar to previous runs, the objectives included the continuation of the feasibility study of utilizing hyacinths as a method for destroying  $\text{N}_2\text{O}_4$  wastes and observing for potential problem areas in operating such a pond.

Setting up the pond of 10,000 gallons required that six liters of pure  $\text{N}_2\text{O}_4$  be added to the pond. A critical point was made in keeping the pH within tolerable limits for the hyacinths. This was accomplished by adding two gallons of 5% NaOH for a pH of 9.2. This pH was lowered to 4.4 with the addition of 6 liters of pure  $\text{N}_2\text{O}_4$ . The final pH of 5.4 was established by adding one more gallon of 5% NaOH. Refer to Chart 5.

Chart 5. Analytical Data for Run C-1 PDP

Days	NO <sub>3</sub> <sup>-</sup> (ppm)	NO <sub>2</sub> <sup>-</sup> (ppm)	NH <sub>4</sub> <sup>+</sup> (ppm)	Total Nitrogen	O-PO <sub>4</sub> (ppm)	D.O. (mg/l)	pH	Turbi- dity F.T.U.	True Color
0	268.4	108.9	1.63	95.38	28.0		5.4	120	500 <sup>±</sup>
+1	281.6	111.4	1.46	98.95	27.25		5.55	35	
+7	140.8	56.1		50.34	22.50		7.3	120	325
+13	44.0	23.9	1.65	18.60	17.00		7.1	150	400
+19	0.13	0.33	1.16	1.08	20.75		6.8	260	85
+28	0.88	0.007	1.57	1.49	18.00		6.6	245	60

The run required a duration of 28 days during which the NO<sub>3</sub><sup>-</sup> was reduced from 268.4 to 0.88 and the NO<sub>2</sub><sup>-</sup> from 108.9 to 0.007. The NH<sub>4</sub><sup>+</sup> fluctuated from 1.6 at the start to 1.57 at the end. The TN decreased from 95.38 to 1.49 ppm, and the O-PO<sub>4</sub> was appreciably slow in uptake with a starting concentration of 28.0 and final of 18.00 ppm.

The turbidity and true color were initially high due to a very dense population of algae amongst the hyacinths. These values dropped with decrease of algae due to the high concentration of N<sub>2</sub>O<sub>4</sub> added to the pond. The turbidity and true color increased as the algae started to reflourish.

Hyacinth coverage was initially 45% and steadily increased to 99% at the end of the run.

If allowed to grow without harvesting, the hyacinths soon out grow their containment (100%+ coverage).

Run #C-3 was organized and operated with these objectives:

- 1) To observe the feasibility of utilizing hyacinths as a method for destroying possible scrubber waste.
- 2) For determining the  $\text{NO}_3^-/\text{NO}_2^-$  levels of this possible waste and its subsequential summer rate of uptake by water hyacinths.

The run was started with addition of 50 gallons of 5% NaOH solution which has been reacted with six liters of  $\text{N}_2\text{O}_4$  to 8600 gals. water in the pond. This simulated the addition of  $\text{N}_2\text{O}_4/\text{NaOH}$  vapor scrubber liquor waste to a hyacinth pond under the "worst condition," i.e. high  $\text{NO}_3^-$ , high  $\text{NO}_2^-$ , and high pH. It was noted that the hyacinth survived the shock of the high  $\text{NO}_3^-/\text{NO}_2^-$  but the algae and pond fauna (insects, snails, and tadpoles) did not. Refer to Chart 6.

Chart 6. Analytical Data for Run C-3 PDP

Days	$\text{NO}_3^-$ (ppm)	$\text{NO}_2^-$ (ppm)	$\text{NH}_4^+$ (ppm)	Total Nitrogen	O- $\text{PO}_4$ (ppm)	D.O. (mg/l)	pH	Turbi dity F.T.U.	True Color
0	237.6	83.3	3.54	82.15	4.33	T 8.0 B 2.0	10.2	115	305
+3	220.0	85.8	4.15	79.4	6.7	T 3.8 B 0.4	9.2	105	345
+10	213.4	72.6	4.03	73.8	7.7	T 4.0 B 0.0	7.95	67	210
+17	37.0	21.5	1.22	15.9	5.3	T 9.0 B 9.0	8.4	85	220
+24	30.8	0.264	2.68	33.7	3.9	T 4.0 B 0.4	7.9	85	280
+31	31.7	0.237	3.48	10.1	3.83	T 10.0 B 9.0	7.8	108	345
+35	6.6	0.554	3.29	4.4	0.58	T 4.0 B 0.0	7.8	90	340
+38	3.96	0.244	4.88	5.0	0.40	T 3.0 B 0.0	8.3	90	300



This run was completed in 35 days. The  $\text{NO}_3^-$  was reduced from 237.6 to 3.96 ppm, the  $\text{NO}_2^-$  was reduced from 83.3 to 0.554 ppm, and the  $\text{NH}_4^+$  fluctuated starting at 3.54 and ending with 4.88. There was a drastic reduction at 17 days into the run when the  $\text{NO}_3^-/\text{NO}_2^-$  dropped from 213.4/72.6 to 37.0/21.5 ppm, respectively.

The initial  $\text{O-PO}_4$  reading of 4.33 was established by the addition of 500 ml of  $\text{H}_3\text{PO}_4$  to the  $\text{N}_2\text{O}_4/\text{NaOH}$  solution. This was reduced to 0.58 ppm.

The pH of 10.2 was high due to the excess of NaOH in the solution. This was lowered by the natural buffering action of the hyacinths.

The turbidity and true color remained about their initial levels due to the large quantity noted in the pond waters.

There was a substantial reduction of TN from 82.15 to 5.0. This calculates to a summer uptake rate of 20.5 lbs TN per acre-day.

The hyacinths grew well on the  $\text{N}_2\text{O}_4/\text{NaOH}$  solution with a minimum of supervision, which was primarily for harvesting and sample collection.

At the present, Run B-5 is under progress. This run is to evaluate the reduction of  $\text{NO}_3^-/\text{NO}_2^-$  when a scrubber solution of .5% NaOH/ 18%  $\text{Na}_2\text{SO}_3$  reacted with  $\text{N}_2\text{O}_4$  is added to the pond. This material is more than likely to be the actual composition of the oxidizer scrubber waste during the Shuttle era. Since sodium sulfite is a strong reducing agent, a considerable COD problem comes about when the scrubber liquor is discharged to the pond. It is hoped that aeration aids the hyacinths absorption of this oxidizer scrubber wastes.

Based on this study the following overall conclusions were drawn:

(1) Water hyacinth readily assimilate from a dilute solution soluble nitrogen - containing compounds, including  $N_2O_4$ , MMH and/or their hydrolysis and/or other reactions products.

(2) The feasibility of the hyacinth pond concept as the ultimate method for destroying  $N_2O_4$  or MMH wastes was fully demonstrated by this investigation.

(3) Nitrogen compound absorption by hyacinth in a pond provides a low cost and efficient means for disposing of  $N_2O_4$  wastes generated at KSC. The hyacinth mats are ultimately disposed of by the low cost sanitary landfilling method rather than harvesting for use as a proteinaceous animal additive. This in large part being due to the very low volume of hyacinth produced in a one, or at most a few, acres of pond surface.

(4) The seasonal influence of temperature does affect the TN uptake rate. Spring has the best growth with a TN uptake rate of 41.5 lbs/day-acre, followed by the summer and fall with 20.5 lbs/day-acre and 16.4 lbs/day-acre. Last is the TN uptake rate of 9.8 lbs/day-acre for winter in spite of the freezing problems encountered. Refer to Chart 7.

Chart 7. UPTAKE RATES

Season	Lbs Total Nitrogen Per Day - Acre	Comments
Winter	9.8	Freeze Damage to Hyacinth.
Spring	41.5	Period of Greatest Growth
Summer	20.5	
Fall	16.4	

(5) Follow up work is necessary to optimize the operating procedures for both  $N_2O_4$  and MMH for application at NASA and for environmental concerns.